

# THE USE OF ALUM MIXTURES FOR REMOVAL AND DECONTAMINATION OF VX AND QL IN AQUEOUS SOLUTIONS

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## Abstract

Truly environmentally friendly means of detoxifying chemical warfare agents have yet to be developed. Toward this end, O-ethyl-S-[2-(diisopropylamino)ethyl] methylphosphonothiolate (VX) and its precursor, O-ethyl-O’-[2-isopropylamino)ethyl] methylphosphonite (QL), were treated with aqueous aluminum sulfate (alum), sodium aluminate, or mixtures of the two. The mixtures were prepared by combining varying volumes of the aqueous salts to give buffered solutions (pH 2-12). Reactions were tracked using phosphorus-31 nuclear magnetic resonance (NMR) and gas chromatography/mass spectrometry (GC/MS). Diazinon and malathion were also investigated. The focus here was on acidic buffers and un-buffered alum because VX and QL were not readily soluble in basic buffers, and because of evidence for the production of the extremely toxic sodium salt of S-[2-(diisopropylamino)ethyl] methylphosphonothioic acid (EA-2192) under basic conditions in the case of VX hydrolysis. Acidic alum and alum buffers hydrolyzed QL within a few minutes. NMR spectra of QL hydrolysate showed two to three broad peaks that are speculated to be different aluminum complexes of methylphosphinic acid based on proton coupled spectra. Acidic alum and alum buffers removed anywhere from 50% to 70% VX within the first twenty minutes from reaction mixtures in NMR tubes. No evidence of EA-2192 production was observed, and the main hydrolysis product, ethyl methylphosphonic acid, was also precipitated from solution. Studies with larger stoichiometric excesses of alum relative to agent are currently under way, but it appears that acidic alum and alum buffers may provide an effective alternate method for the destruction of QL and potentially VX as well.

## INTRODUCTION

Results of earlier studies using aqueous aluminum sulfate (alum) and aluminum sulfate buffered with sodium aluminate demonstrated potential for the destruction of G-class nerve agents in a more environmentally friendly fashion than methods currently employed.<sup>1</sup> Here, we report efforts to further characterize the reactions of organophosphorus compounds with alum solutions. These investigations involve QL, VX, malathion and diazinon. Preliminary investigations were also carried out using reaction columns made up of aluminum sulfate octadecahydrate flushed with 1.0 M alum solution.

## EXPERIMENTAL

Alum buffers were made *in situ* by mixing different volumes of 1.0 M  $\text{Al}_2(\text{SO}_4)_3$  and 1.0 M  $\text{NaAlO}_2$  in the ratios shown in Figure 1. Alum and alum buffers were reacted with simulants

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and agents in 5 mm NMR tubes as described before.<sup>1</sup>. For this work, VX reactions were in doubly-contained NMR tubes and employed 5  $\mu$ L agent and 500  $\mu$ L alum solution.

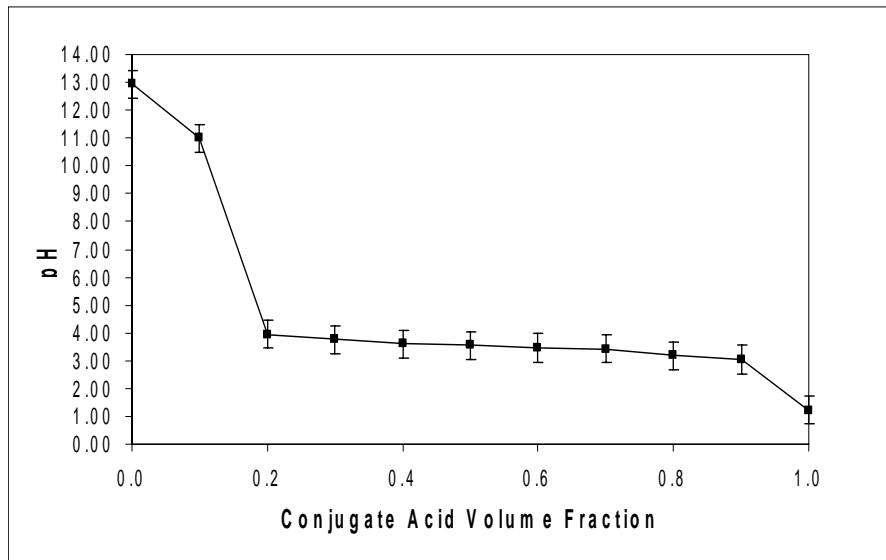


Figure 1. Alum buffer pH as a function of conjugate acid volume fraction

Time course experiments were conducted on varying amounts of QL, malathion, and diazinon using only acid buffers. Experiments were conducted on QL at pH = 2, 3, and 4. Malathion and diazinon were treated with pH 4 buffer. VX reactions were carried out with four different alum solutions: 1.0M  $\text{Al}_2(\text{SO}_4)_3$ , 1.0 M  $\text{NaAlO}_2$ , pH 4 buffer and pH 3 buffer. VX results are reported in % of original concentration based on comparison with external standards. In the case of QL, concentrations are reported as integration areas. Reactions on VX and QL were monitored with  $^{31}\text{P}$ -NMR over various time frames ranging from less than 30 minutes to several days. Some studies used hexamethylphosphoramide (HMPA) as an internal standard.

Methylphosphinic acid derived from decontaminated QL solutions (50  $\mu$ L, concentration unknown) was treated separately with 5 mL volumes of 1.0 M  $\text{Al}_2(\text{SO}_4)_3$ , alum buffer pH 4, and deionized water as a control. Samples were centrifuged and 700  $\mu$ L aliquots were used to acquire the  $^{31}\text{P}$ -NMR spectra.

All NMR experiments were  $^{31}\text{P}$ -detected, proton inverse gated decoupled. NMR experiments were collected on samples prepared directly in NMR tubes as described above using a Bruker AVANCE 300 MHz NMR spectrometer fitted with 5 mm broadband probe. All spectra were referenced to external  $\text{H}_3\text{PO}_4$  (1% (v/v) in  $\text{D}_2\text{O}$ ; 0 ppm). The detection limits were 0.1% of initial analyte concentration. For each spectrum, the reaction time was taken to be the midpoint of the data acquisition period of 10.2 minutes. Initial spectra were obtained within the first fifteen minutes after mixing.

## RESULTS AND DISCUSSION

### *Simulant Results*

Neither malathion nor diazinon were soluble enough in the acidic buffers to react. Obvious layers of simulant were observed on top of the buffer floc. Earlier studies have shown

the basic buffer to be effective on malathion<sup>1</sup>. Diazinon was not tested in the earlier study. Another VX simulant, *O,S*-dimethyl phenylphosphonothioate,<sup>2</sup> is currently under investigation.

### QL Results

QL reacts within twenty minutes when exposed to 1.0 M  $\text{Al}_2(\text{SO}_4)_3$  or alum buffers at pH 2, 3, and 4. No QL peak was observed in the  $^{31}\text{P}$ -NMR spectra, but the peaks from two hydrolysis products, ethyl methyl phosphinate (EMP,  $\delta$  45.7 ppm) and diisopropylaminoethyl methyl phosphinate (DMP,  $\delta$  43.3 ppm), were seen. These two peaks slowly decreased in intensity while three broad peaks discussed further in the section below grew in intensity. Table 1 shows the half-lives for EMP and DMP as a function of pH.

The final products are suspected to be three different aluminum complexes of methyl phosphinic acid (MP), with broad peaks centered at  $\delta$  33.7, 23.1, and 21.7 ppm. Ester products were assigned by comparison with published chemical shifts<sup>3</sup>, and all phosphinic acid derivatives were confirmed with proton coupled  $^{31}\text{P}$ -NMR spectra. Reaction rates were in agreement with literature observations<sup>3</sup> to the extent that EMP disappears more rapidly than DMP. The EMP half-life was inversely proportional to pH, a trend which is also consistent with the observations of Verweij, *et al.*<sup>3</sup> There was no clear trend with respect to pH for DMP, however, and the identities of the MP aluminum complexes are still under investigation.

Table 1. Half-lives (hr) of QL hydrolysis products, DMP and EMP.

Treatment Solution	EMP	DMP
1.0 M $\text{Al}_2(\text{SO}_4)_3$ (pH = 1.2)	3.0	15
Alum Buffer pH = 2	2.0	30
Alum Buffer pH = 3	1.0	10
Alum Buffer pH = 4	1.0	20

One method of destroying QL has been to employ a 0.3% NaOH solution at 38<sup>o</sup> C for hydrolysis. QL is not very soluble in base, and the resultant biphasic system can affect the kinetics. The alum treatment described above was so rapid that no evidence of QL was found in the initial NMR spectra, thus making kinetics studies for the disappearance of QL nearly impossible.

The identities of the MP aluminum complexes are still under investigation. Figure 2a shows a  $^{31}\text{P}$ -NMR spectrum of a reaction mixture of MP in 1.0 M  $\text{Al}_2(\text{SO}_4)_3$ . For comparison, Figure 2b shows a control spectrum of MP in water, and Figure 2c shows a QL reaction mixture in pH 3 alum buffer after 3 days. Except for the impurity peak and the residual EMP peak, the treated QL spectrum closely correlates to alum-treated MP shown in Figure 2a. Figure 3 shows the reaction time profile in pH 2 alum buffer.

Experiments on MP alone with a large molar excess of alum and alum buffer (pH 4), followed by centrifugation, showed that virtually all of the MP was removed from solution as evidenced by  $^{31}\text{P}$ -NMR spectra (Figure 2d).

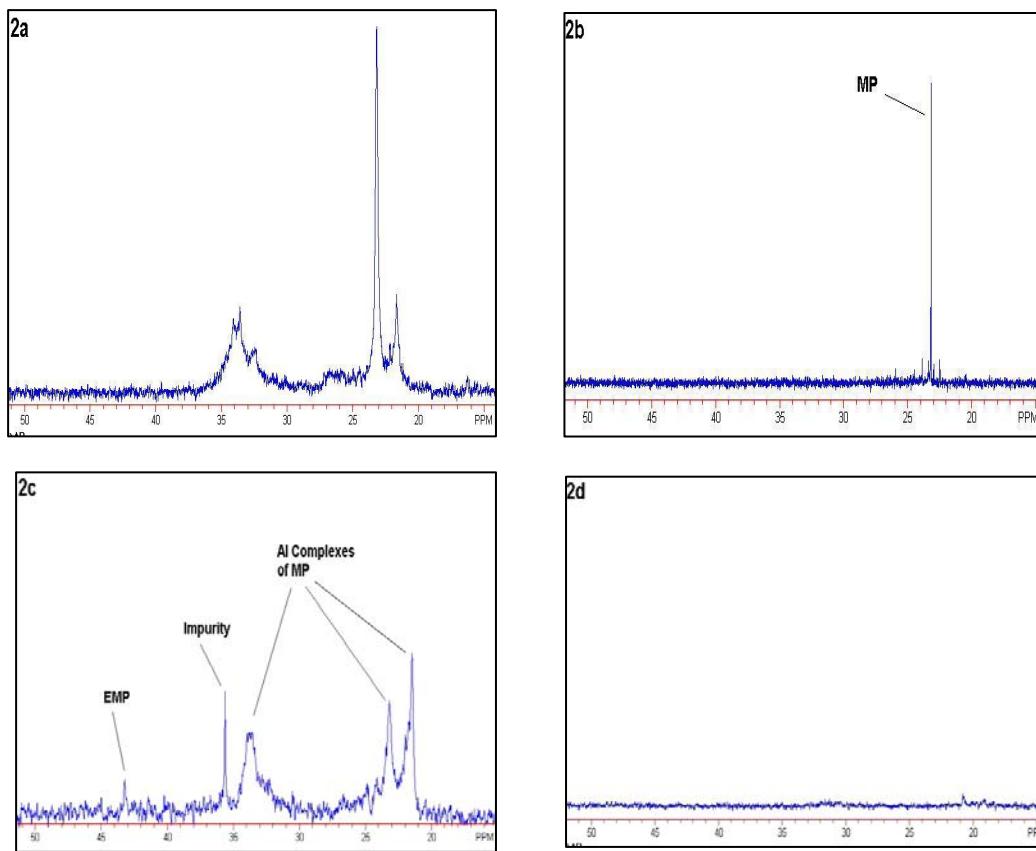


Figure 2.  $^{31}\text{P}$  NMR spectra of: a) MP reaction mixture in 1.0 M  $\text{Al}_2(\text{SO}_4)_3$  compared to b) untreated MP and c) QL reaction mixture in pH 3 alum buffer after 3 days. d)  $^{31}\text{P}$  NMR spectrum of reaction mixture of MP treated with large molar excess of  $\text{Al}_2(\text{SO}_4)_3$ .

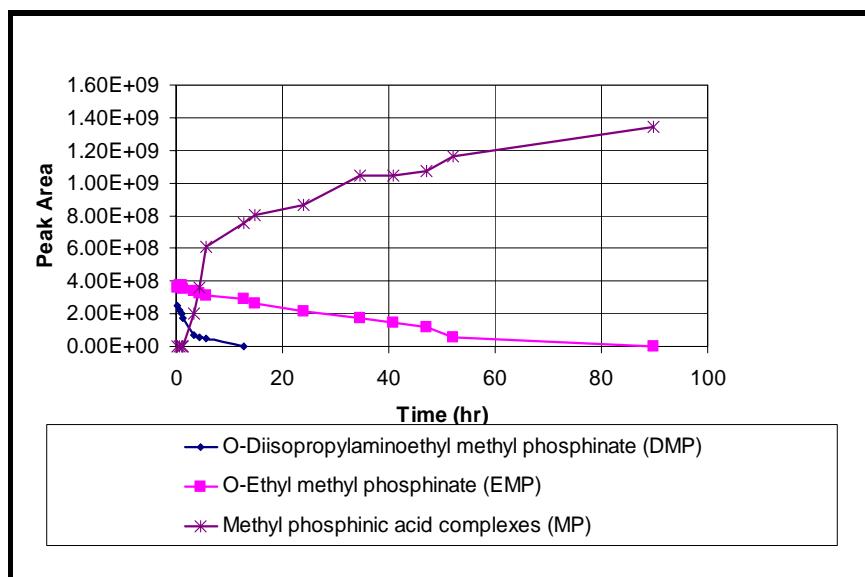


Figure 3. QL reaction time profile in pH 2 alum buffer.

## VX Results

Table 2 shows initial rates of decrease of residual VX upon treatment with 1.0 M  $\text{Al}_2(\text{SO}_4)_3$ , alum buffer pH 4 (50/50 mixture), and 1.0 M  $\text{NaAlO}_2$ . Figure 4 shows the typical slow decrease of VX concentration in alum buffer pH 4 (50/50 mixture) after the relatively quick initial loss in the first few minutes. VX has a half-life of 5 days for agent remaining after initial loss. Even though basic  $\text{NaAlO}_2$  gave the best results for initial decontamination (> 95% loss), the  $^{31}\text{P}$ -NMR spectrum showed (Figure 5a) the presence of the very toxic basic hydrolysis product, EA2192 (sodium S-[2-(diisopropylamino)-ethyl] methylphosphonothiolate), assigned based on reported chemical shifts.<sup>4</sup> Further study of basic reagent was abandoned for this reason.

Table 2. Initial loss rates and remaining half-lives (days) of residual VX treated with Alum solutions.

Treatment Solution	Initial Loss	VX Half Life
1.0 M $\text{Al}_2(\text{SO}_4)_3$	66.6%	34 d
Alum Buffer pH = 4	49.7%	5 d
1.0M $\text{NaAlO}_2$	97.3%	Not measured

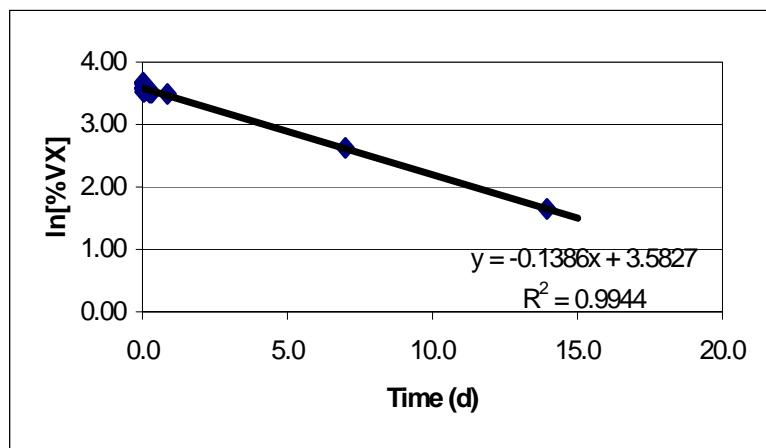


Figure 4. Loss of VX over time after initial reaction in buffered alum solution at pH 4 ( $\ln[\% \text{VX}]$  vs time in days)  $t_{1/2} = 5$  days.

Time course experiments with VX in 1.0M  $\text{Al}_2(\text{SO}_4)_3$  showed an initial loss of 66.6% of the original concentration, but a half-life of 34 days for the remaining VX. In all cases, however, the principle hydrolysis product, ethyl methylphosphonic acid (EMPA) is taken out of solution (Figure 5b).

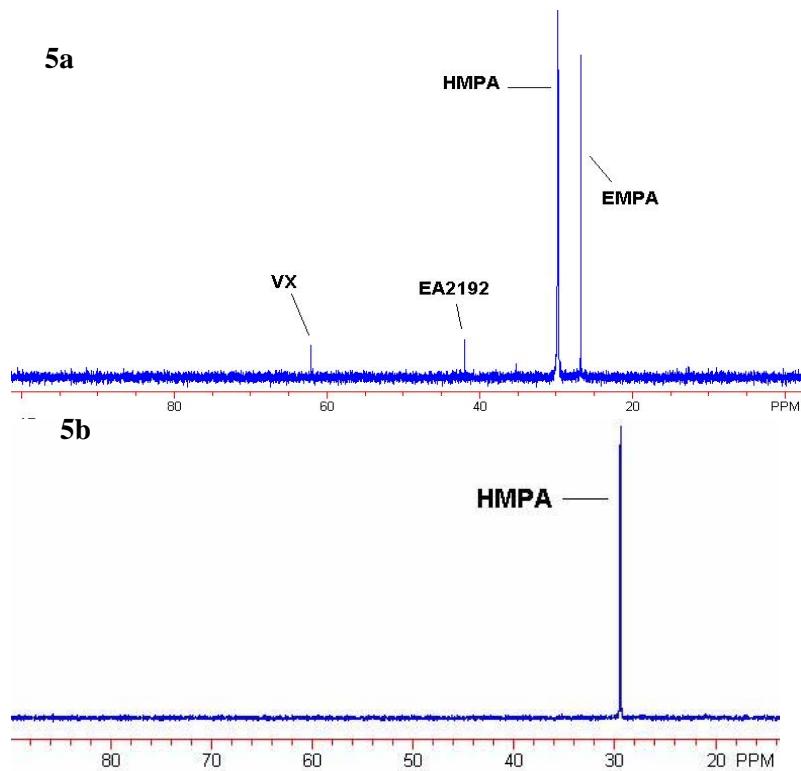


Figure 5: <sup>31</sup>P NMR spectra of: a) VX treated with 1.0 M NaAlO<sub>2</sub> (pH ~12.5). b) VX treated with pH 4 alum buffer after 12 days.

#### CONCLUSIONS AND FUTURE DIRECTIONS

Alum treatment appears to be the method of choice for destruction of QL. The process destroys QL more rapidly than basic methods, no biphasic mixtures are encountered, and the methylphosphinic acid complexes are completely removed from solution.

Acidic alum solutions are also effective for destroying VX. Alum buffer pH 4 appears to be most effective for initial destruction of VX and subsequent removal of EMPA from solution without production of EA2192. Other organophosphorus agents and simulants as well as mustards are currently under investigation since earlier studies showed alum to be effective on removal of GD.<sup>1</sup> Reaction column experiments (~10 mL solid alum bed volume) are underway with alum present at  $\geq$  100-fold excess over agent.

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